# COOPERATIVE INVESTIGATION OF ACCEPTANCE TEST METHODS FOR CHEMICAL ANALYSIS OF POZZOLANS FOR MAHOR OXIDES

Leonard Pepper

Army Engineer Waterways Experiment Station
Vicksburg, Mississippi

August 1964

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## PREFACE

The investigation reported herein was authorized by the Office, Chief of Engineers, by first indorsement dated 26 January 1960 to a letter from the U. S. Army Engineer Waterways Experiment Station (WES) dated 20 January 1960, subject, "Project Plan for Research in Mass Concrete - Investigation of Cement-Replacement Materials - Investigation of Chemical Acceptance Tests for Pozzolans," and formed part of the Engineering Studies Program, Item ES 601.

The work was conducted at the following four laboratories:

a. Bureau of Public Road (BPR) under the direction of Mr. Harold Allen, Chief, Division of Physical Research.

b. National Bureau of Standards (NBS) under the direction of Mr. R. L. Blaine, Chief, Concreting Materials Section.

c. Bureau of Reclamation (BR) under the direction of Mr. W. H. Price, Chief, Division of Engineering Laboratories.

d. WES under the direction of Mr. T. B. Kennedy, Chief, Concrete Division.

This report was prepared by Mr. Leonard Pepper, Concrete Division, WES.

Col. Edmund H. Lang, CE, and Col. Alex G. Sutton, Jr., CE, were Directors of the WES during conduct of the investigation and the preparation and publication of this report. Mr. J. B. Tiffany was Technical Director.

CONTENTS

## SUMMARY

The procedure specified in acceptance testing of pozzolans for chemical analysis for major oxides is more involved and more costly than the procedure used for such analyses in the acceptance testing of portland cement. In order to investigate the simplification of the procedure for testing pozzolans, four pozzolans were evaluated by each of four laboratories using three test methods. The methods were:

a. Method A, the prescribed method, which involves fusing the sample and then determining the major oxides by the referee procedure for portland cement,

b. Method B, which consists of pretreating the sample as in Method A, determining the amount of $SiO_2$ by the referee procedure but omitting the second evaporation, and determining the remaining constituents by the optional procedure for portland cement,

c. Method C, which involves igniting the sample and determining the constituents by the optional procedure for portland cement.

The results of the study indicated that:

a. There was no significant difference between the methods in determining MgO.

b. There was a significant difference between the methods in determining $SiO_2$. The highest values for $SiO_2$ content were obtained using Method A and the lowest were obtained using Method C; thus Method A was the most effective in separating $SiO_2$ from the other constituents in the sample, and Method C was the least effective.

c. There was no significant difference between Methods A and C in determining $R_2O_3$, whereas there was a significant difference between Methods A and B. The $R_2O_3$ content determined by Method B was higher than that determined by either of the other two methods.

d. There was no significant difference in the sum of $SiO_2$ and $R_2O_3$ determined by Methods A and B. However, the sum of

$SiO_2$ and $R_2O_3$ determined by Method C was significantly lower than that determined by the other methods.

e. The laboratories were biased in the application of Method A in determining $SiO_2$, $R_2O_3$, and MgO, and in the application of Method B in determining $SiO_2$ and MgO.

The chemical requirements for a pozzolan are for the sum of the $SiO_2$ and $R_2O_3$ contents to be greater than 70.0% and for the MgO content to be less than 5.0%. It was found in this study that the sum of the $SiO_2$ and $R_2O_3$ contents obtained by either Method B or C is not significantly greater than the sum obtained by Method A, and also that the MgO content as determined by either Method B or C is not significantly less than the MgO content determined by Method A. Pozzolans that do not meet the chemical requirements when tested using Method A would not be expected to meet these requirements when tested using either Method B or C.

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# COOPERATIVE INVESTIGATION OF ACCEPTANCE TEST METHODS FOR CHEMICAL ANALYSIS OF POZZOLANS FOR MAJOR OXIDES

## PART 1: INTRODUCTION

### Background

1. The procedure for the chemical analysis of pozzolans is outlined in CRD-C 263.[4*] In this procedure, the pozzolan is first ignited, then fused with $Na_2CO_3$, after which the major oxides are determined by applying pertinent portions of the portland cement referee procedure, Method 1101 of CRD-C 209.[4] Thus, the chemical analysis of pozzolans is more involved, more time-consuming, and more costly than the analysis of portland cement.

2. The Federal Test Method Standard No. 158a[3] (CRD-C 209) provides two methods for the analysis of portland cement: the referee procedure, Method 1101, referred to above, and an optional procedure, Method 1111. The latter procedure is simpler and quicker, but possibly less accurate than the former. Therefore, the optional procedure is normally used for routine analysis of cement, and the referee procedure is used in case of dispute or when the results obtained using the optional procedure are so close to the specification limit that the cement's meeting or failing to meet the specification requirement is in doubt.

3. The major differences between the two procedures (Methods 1101 and 1111) in the analysis of portland cement for major oxides are:

a. Silicon dioxide ($SiO_2$) determination.

(1) Method 1101 requires the sample to be digested in a 1:1 HCl solution followed by a double evaporation and filtration to separate $SiO_2$ from the other constituents.

(2) Method 1111 requires the sample to be mixed with $NH_4Cl$ and digested in concentrated HCl containing 1 to 2 drops of $HNO_3$. The resulting gelatinous mass is filtered to separate $SiO_2$ from the other constituents.

b. Calcium oxide (CaO) determination.

(1) Method 1101 requires that manganese be removed from the

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* Raised numerals refer to similarly numbered items in list of references at end of text.

filtrate obtained in the determination of $R_2O_3$.* Calcium is then obtained as a result of a double precipitation and filtration of calcium oxalate, and CaO is determined gravimetrically.

(2) Method 1111 does not require the removal of manganese from the filtrate obtained in the determination of $R_2O_3$. Calcium is obtained as a result of a single precipitation and filtration of calcium oxalate, and CaO is determined by titration with $KMnO_4$.

c. Magnesium oxide (MgO) determination.

(1) Method 1101 requires that magnesium be separated from the filtrate obtained in the CaO determination by a double precipitation and filtration as magnesium ammonium phosphate. MgO is then determined gravimetrically as a pyrophosphate.

(2) Method 1111 requires the filtrate obtained from the CaO determination to be reacted with 8-hydroxyquinoline. The magnesium precipitate is filtered and then redissolved. Potassium bromate bromide is added, and the resulting solution is titrated with $Na_2S_2O_3$ to determine the MgO content of the sample.

4. During the latter part of 1959, in correspondence with the Office, Chief of Engineers (OCE), the U. S. Army Engineer Division Laboratory, North Pacific (NPDL), raised the question of the feasibility of using the applicable portions of Method 1111, rather than Method 1101 as required by CRD-C 263, for routine testing of pozzolans. The National Bureau of Standards (NBS) Seattle Laboratory had informed NPDL that routine analysis of pozzolans using Method 1111 could be performed in one day, whereas doing so by Method 1101 required from three to five days. A change to Method 1111 would result in a considerable saving in the cost of acceptance testing of pozzolans.

5. It was the opinion of chemists associated with the NBS in Washington, when they were consulted by OCE, that the applicable portions of Method 1111 should not be substituted for the present procedure unless considerable supporting data were available to justify such action. They pointed out that Method 1111 had been developed for portland cement, and that the method might not be directly applicable to materials of somewhat

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* In chemical analysis of materials such as those with which this report is concerned, $R_2O_3$ represents principally $Fe_2O_3$ and $Al_2O_3$ not differentiated.

different compositions. They also stated that although the specified procedure for pozzolans, CRD-C 263, is far from perfect, several laboratories devoted a considerable amount of time to developing it, and an appreciable amount of additional work will be needed to improve and perhaps simplify it.

## Purpose and Scope of Investigation

6. At a conference held at the U. S. Army Engineer Waterways Experiment Station (WES) in September 1959 between representatives of OCE and WES, the WES was directed to conduct a cooperative program with three other laboratories to evaluate three analytical procedures in the chemical analysis of pozzolans for major oxides. The investigation was confined to the determination of the $SiO_2$, $R_2O_3$, and MgO contents of four pozzolans. Samples of each of the pozzolans were analyzed for each of these constituents at the NBS (Washington), the Bureau of Public Roads, the WES, and the Bureau of Reclamation* by:

a. The prescribed method, CRD-C 263.

b. By fusing the samples, then using a modification of Method 1101 to determine $SiO_2$, and applicable procedures of Method 1111 to determine $R_2O_3$ and MgO.

c. The applicable procedures of Method 1111, without first fusing the samples.

## Scope of This Report

7. This report describes the materials tested and the test methods used, analyzes the test results, and presents conclusions derived therefrom.

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* These laboratories are referred to hereinafter as laboratories 1, 2, 3, and 4, respectively.

## PART II: MATERIALS AND TEST METHODS

### Materials

8. Of the many pozzolans that may have to be tested to completely evaluate the test procedures, this investigation was confined to four of the 12 pozzolans (one from each of the four principal classes of pozzolans) that were used in Phase A of the Cement-Replacement Investigation program.[5] The four selected pozzolans were:

a. Fly ash (FA III).

b. Natural volcanic glass (Pum F).

c. Calcined opaline shale (C Sh M).

d. Uncalcined diatomite (Unc D).

The constituents of these materials as previously reported[5] are shown in table 1.

9. Each pozzolan was agitated in a 1-pt twin-shell blender for approximately three days to eliminate segregation in the material. Each pozzolan was then quartered to yield four samples of approximately 20 g each; these samples were then sealed in plastic vials. One sample of each of the four pozzolans was sent to each of the cooperating laboratories.

### Test Methods

10. All the samples were ignited, in accordance with paragraph 8(a) of CRD-C 263, prior to either fusing the sample or digesting it with acid and ammonium chloride. Manganese was removed from all the samples as described in Section 4 of Method 1101 of CRD-C 209. All the results were reported on an as-received basis. Each laboratory determined in duplicate the $SiO_2$, $R_2O_3$, and MgO contents of each of the four pozzolans using each of the following test procedures:

a. Method A, the procedure described in CRD-C 263.

b. Method B, in which the sample was fused as directed in paragraph 9(a) through 9(d) of CRD-C 263, except that the silica content was determined using a single evaporation (i.e., the procedures described in the first three sentences of the

second paragraph of the silica determination procedure of Method 1101 of CRD-C 209 were omitted). The $R_2O_3$ and MgO contents were determined using the procedure described in Method 1111 of CRD-C 209.

c. Method C, the procedure described in Method 1111 of CRD-C 209 for determining $SiO_2$, $R_2O_3$, and MgO.

## PART III: ANALYSIS OF TEST RESULTS

### Presentation of Results

11. The test results obtained by the four laboratories are shown in tables 2, 3, and 4, and also in plates 1, 2, and 3. The original results obtained by WES on the pozzolans tested (see table 1) and the results of the present investigation are regarded as being in agreement considering:

a. The variance that can be expected between samples of pozzolan.

b. The variance between operators within a laboratory.

12. Plate 1 shows a general tendency for the $SiO_2$ values to decrease as the procedures were simplified. This tendency is also evident in comparing the average $SiO_2$ values for each method, which were: Method A, 61.08%; Method B, 59.93%; and Method C, 58.22%.

13. The effect of the methods on the $R_2O_3$ values is not clearly evident (see plate 2). However, with several exceptions, the results obtained for $R_2O_3$ with Method B are higher than the results obtained with Method A, whereas the results obtained with Method C are equal to or less than the Method A results. This variation is also suggested by the average values of $R_2O_3$ for each method, which were: Method A, 20.21%; Method B, 20.93%; and Method C, 19.83%.

14. Plate 3 does not suggest any specific relation between the methods and the MgO values; however, the MgO results obtained by laboratory 2 are significantly different from the results obtained by the other laboratories. The average values of MgO for each method used were: Method A, 1.00%; Method B, 0.97%; and Method C, 0.90%.

### Evaluation of Results by Study of Error Variance

15. The significance of the effects of the methods, described in paragraphs 12-14, on the resultant averages can be most readily evaluated by subjecting the data to an analysis of variance. For the results of the analysis to have physical meaning, it is essential that the error variance of the data be homogeneous when considered among materials, among

laboratories, or among methods. The error variance (within-laboratory variance) was calculated directly from the duplicate results, and is shown in tables 2, 3, and 4. Also shown in tables 2, 3, and 4 is the pooled error variance among laboratories and within methods and within materials. The homogeneity of the error variances was tested by means of a modification of the Bartlett Test.* [2] Only six out of 143 variances differed from the other members of the group at the 95% confidence level. They were:

| Constituent | Material | Method | Laboratory |
|---|---|---|---|
| $SiO_2$ | FA III | B | 4 |
| $SiO_2$ | C Sh M | B | 4 |
| $SiO_2$ | Unc D | B | 2 |
| $R_2O_3$ | FA III | C | 3 |
| MgO | C Sh M | B | 1 |
| MgO | Unc D | C | 1 |

The following observations can be made concerning these deviations:

a. The deviations were due to the variances being higher than those of other members of the group.

b. None of the deviations occurred when Method A was used.

c. At least one deviation was found for each laboratory.

16. The resultant pooled variances, which are the error variances for materials within a test method, are also shown in table 5. These variances were pooled to determine the error variance for the test methods. Only one, the error variance for $SiO_2$ content of Pum F as determined by Method B, was found to be significantly greater at the 95% confidence level than the other variances of the group, and was therefore not included in the calculations to determine resultant pooled variance.

17. The precision of the three test methods is compared in table 6. The variances of the three methods for the determination of $SiO_2$ differ significantly at the 95% confidence level and cannot be pooled. The error variance found for the $SiO_2$ determination using Method B is

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* The modification of the Bartlett Test used in the analysis reported here is taken from Davies.[2] In a previous study[6] the form of the Bartlett Test used to examine error variance for homogeneity was that given by Youden.[7] The Davies modification was regarded as more appropriate for use with the data derived from this investigation.

significantly lower than that for Method A. The greater precision of Method B is probably due to the number of variances which were excluded as being significantly excessive during the calculation of the variance. It is believed that additional work would indicate that the error variance of Method B is the same as or even greater than the error variance of Method A. The variance of Method A in the determination of $R_2O_3$ is significantly less at the 95% confidence level than that of the other two methods, and therefore cannot be pooled with them. The precision of the three methods in the determination of MgO is essentially the same and the three variances are pooled. An analysis of variance can be applied to all the data obtained in the determination of MgO, but not to all the data obtained in either the $SiO_2$ or $R_2O_3$ determination. The analysis of variance cannot be used to determine the significance of the effect of methods on the determination of either $SiO_2$ or $R_2O_3$.

18. The resultant pooled error variances are compared in table 7 with the error variances reported by the National Bureau of Standards[1] as a result of an interlaboratory study conducted on portland cements. Table IX of the report gives values for standard deviation attributable to the precision of the method used to obtain the test result and values for the standard deviation of the test results for 12 samples. The value for standard deviation attributable to the precision of the method used is designated a/2 and is obtained graphically. Values from table IX for $SiO_2$, $Al_2O_3$, and MgO have been squared to permit comparison with variance values developed in the present investigation and are given in table 7 of this report. All the variances determined in the investigation reported herein are less than those computed from the values for standard deviation reported in reference 1 as the average of 12 samples, except for the variance of the $SiO_2$ determination by Method C. It should be noted that Method C was used for the analysis of portland cement in the NBS interlaboratory study and that the pozzolans analyzed in the investigation reported herein can normally be expected to have a greater variance than portland cement, particularly in the determination of $SiO_2$. The error variances for the determination of MgO by all three test methods, $R_2O_3$ by Method A, and $SiO_2$ by Method B are all less than the respective variances calculated from the reported values of a/2. The error variances

determined in this investigation can therefore be considered to be equal to or less than the error variances that can normally be expected in the analysis of portland cement.

## Analysis of Results by Ranking of Laboratories

19. The data shown in tables 2-4 and plates 1-3 can also be examined by a method reported by Youden.[8] In this analysis, the average value obtained by a laboratory was ranked with respect to the results obtained by the other laboratories for the same material, method, and constituent. A score of 1 was given to the laboratory having the highest result, 2 to the next highest, 3 to the next highest, and finally a score of 4 to the laboratory having the lowest result. These scores were summed for the four materials analyzed by each method and are shown in table 8. The minimum score that can be obtained by any laboratory is 4, and the maximum is 16. Both of these scores are significant at the 5% probability level. A score of 4 signifies that the laboratory had the highest results in the analysis of all four materials, whereas a score of 16 signifies that the laboratory had the lowest results in the analysis of all four materials. The average expected score is 10. If the rankings of the laboratories are randomly distributed, the expected sum of squares (S') is 20. The ratio of the calculated to the expected sums of squares (S/S') will indicate whether the rankings of the laboratories are randomly distributed. A ratio equal to or greater than 2.60 indicates that the laboratory rankings are significantly different from random at the 5% probability limit, and a ratio equal to or greater than 3.78 is significant at the 1% probability limit.

20. As can be seen in table 8, the test results obtained by laboratory 2 tend to be low in the determination of $SiO_2$ and MgO. Laboratory 3 tends to produce low $R_2O_3$ results. The results obtained by laboratory 1 in the determination of $SiO_2$ by Methods A and B are high, whereas the test results obtained by laboratory 4 in the determination of $R_2O_3$ and MgO using Method A are high. The distribution of the rankings of the laboratories is significantly different from random for all determinations using Method A and also for the determination of $SiO_2$ and MgO using Method B. These results imply a definite laboratory bias and a significant between-laboratory variance.

## PART IV: CONCLUSIONS

21. Analysis of the test results indicates that the test methods had no effect on the results obtained in the determination of MgO. The precision of the three test methods was the same, and the differences between the means are not significant since the 95% confidence intervals overlap: Method A, 1.07 to 0.93%; Method B, 1.04 to 0.90%; and Method C, 0.97 to 0.83%.

22. The test methods did have an effect on the results obtained in the determination of $SiO_2$. The precision of the three methods was different. The largest variance occurred in Method C and the least variance in Method B, although it is believed that the variance of Method B should be larger than indicated in this study and equal to or greater than that of Method A. The differences between the means are also significant since the 95% confidence intervals do not overlap: Method A, 61.45 to 60.71%; Method B, 60.08 to 59.78%; and Method C, 58.94 to 57.50%. Method A is, therefore, the most effective method in separating $SiO_2$ from the other constituents in the sample, and Method C is the least effective.

23. The test methods also had an effect on the results obtained in the determination of $R_2O_3$. The precision of Methods B and C was found to be the same. The precision of Method A was found to be different and greater than that of the other two methods. The mean value obtained for $R_2O_3$ using Method B was significantly greater than that obtained with either Method A or C, whereas there was no significant difference between the means obtained with Methods A and C. The 95% confidence intervals were: Method A, 20.37 to 20.05%; Method B, 21.28 to 20.58%; and Method C, 20.18 to 19.48%.

24. Although the $SiO_2$ content as determined by Method B is significantly less than that determined by Method A, the $R_2O_3$ content determined by Method B is significantly greater than that determined by Method A. As a result, the sum of $SiO_2$ and $R_2O_3$ as determined by Method B is not significantly different from the sum determined by Method A. However, the sum of $SiO_2$ and $R_2O_3$ as determined by Method C is significantly less than the sum determined by Method A. Assuming that the variances may be summed to obtain the variance of the sum of $SiO_2$ and $R_2O_3$, the 95% confidence

intervals were: Method A, 81.69 to 80.89%; Method B, 81.24 to 80.48%; and Method C, 78.85 to 77.25%.

25. The precision of the laboratories conducting this study was high, surpassing the precision that is normally attained in the analysis of portland cement, except for the precision obtained in the determination of $SiO_2$ using Method C. The precision can be expected to be materially less during routine acceptance testing. However, it is not expected that the reduction in precision would affect the conclusions reached in this investigation.

26. The laboratories were biased in the application of Method A in the determination of all three constituents. The laboratories were also biased in the application of Method B in the determination of $SiO_2$ and MgO. Further work will be necessary to determine the particular parts of the procedures used in Methods A and B that permit the results obtained by the different laboratories to deviate from each other.

27. The chemical requirements for a pozzolan are for the sum of the $SiO_2$ and $R_2O_3$ contents to be greater than 70.0% and for the MgO content to be less than 5.0%. It was found in this study that the sum of the $SiO_2$ and $R_2O_3$ contents obtained by either Method B or C is not significantly greater than the sum obtained by Method A, and also that the MgO content as determined by either Method B or C is not significantly less than the MgO content determined by Method A. Pozzolans that do not meet the chemical requirements when tested using Method A would not be expected to meet these requirements when tested using either Method B or C. Both Methods B and C are, therefore, suitable for use as optional methods for acceptance testing of pozzolans. Method C is the more economical to perform, and would generally be the preferred optional method. However, the sum of $SiO_2$ and $R_2O_3$ contents obtained by Method C is significantly less than the sum obtained by Method A; therefore, the use of Method C may require extensive retesting for pozzolans that just meet the chemical requirements. This can best be illustrated with the values obtained for C Sh M in this study. Of the four pozzolans tested, the sum of the $SiO_2$ and $R_2O_3$ contents of C Sh M was the closest to the specification limit. The following average values were reported:

Sum of $SiO_2$ and $R_2O_3$ Contents of C Sh M, %

| Method | Lab 1 | Lab 2 | Lab 3 | Lab 4 |
|---|---|---|---|---|
| A | 72.69 | 70.68 | 71.79 | 72.72 |
| B | 72.98 | 70.52 | 71.01 | 71.80 |
| C | 69.45 | 68.72 | 70.17 | 70.66 |

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Table 1

Results of Chemical Tests of Pozzolans*

| Constituent, % | FA III | Pum F | C Sh M | Unc D |
|---|---|---|---|---|
| $SiO_2$ | 38.2 | 68.8 | 61.2 | 76.7 |
| $Al_2O_3$ | 25.7 | 14.8 | 12.5 | 12.0 |
| $Fe_2O_3$ | 16.3 | 1.4 | 4.5 | 2.2 |
| CaO | 3.9 | 0.65 | 8.6 | 0.60 |
| MgO | 0.9 | 0.33 | 3.0 | 0.70 |
| $SO_3$ | 0.60 | 0.03 | 0.44 | 0.05 |
| Ignition loss | 12.2 | 3.9 | 6.8 | 3.2 |
| $Na_2O$ | 0.63 | 1.38 | 0.88 | 1.72 |
| $K_2O$ | 1.02 | 4.96 | 1.14 | 1.68 |
| Total as $Na_2O$ | 1.30 | 4.64 | 1.63 | 2.83 |
| $P_2O_5$ | 0.26 | 0.02 | 0.29 | 0.29 |
| $Mn_2O_3$ | 0.16 | 0.05 | 0.08 | 0.03 |
| Insoluble residue | 64.9 | 94.6 | 67.1 | 76.2 |
| Moisture content | 0.17 | 0.83 | 1.7 | 4.1 |
| Sulfide sulfur | 0.13 | 0.00 | 0.00 | 0.09 |
| Total carbon | 11.13 | 0.02 | 1.10 | 0.15 |

* Results of tests by WES, using Method A, reported in 1955.[5]

Table 2

$SiO_2$ Test Results

| Method | Material | Test Run | $SiO_2$ in Percent as Measured at Laboratory 1 | 2 | 3 | 4 | Pooled Variance* | Resultant Pooled Variance After Bartlett Test | Degrees of Freedom Associated with Resultant Variance |
|---|---|---|---|---|---|---|---|---|---|
| A | FA III | 1 | 38.38 | 37.28 | 37.71 | 38.08 | - | - | |
| | | 2 | 38.50 | 37.15 | 37.79 | 38.16 | - | - | |
| | | Variance | 0.0072 | 0.0084 | 0.0032 | 0.0032 | 0.0055 | 0.0055 | 4 |
| | Pum P | 1 | 71.86 | 70.11 | 70.76 | 71.85 | - | - | |
| | | 2 | 72.18 | 70.11 | 70.68 | 71.76 | - | - | |
| | | Variance | 0.0512 | 0 | 0.0032 | 0.0040 | 0.0146 | 0.0146 | 4 |
| | C Sa M | 1 | 56.68 | 56.38 | 56.06 | 56.92 | - | - | |
| | | 2 | 57.20 | 56.17 | 56.16 | 56.68 | - | - | |
| | | Variance | 0.1352 | 0.0220 | 0.0050 | 0.0288 | 0.0478 | 0.0478 | 4 |
| | Unc D | 1 | 79.38 | 77.24 | 78.19 | 79.92 | - | - | |
| | | 2 | 80.06 | 77.41 | 77.92 | 79.94 | - | - | |
| | | Variance | 0.2312 | 0.0144 | 0.0364 | 0.0002 | 0.0706 | 0.0706 | 4 |
| B | FA III | 1 | 38.28 | 34.34 | 36.36 | 37.06 | - | - | |
| | | 2 | 38.26 | 34.31 | 36.86 | 37.78 | - | - | |
| | | Variance | 0.0002 | 0.0004 | 0.0050 | 0.2592** | 0.0662 | 0.0019 | 3 |
| | Pum P | 1 | 71.56 | 66.40 | 70.42 | 68.42 | - | - | |
| | | 2 | 71.86 | 66.15 | 70.08 | 68.00 | - | - | |
| | | Variance | 0.0450 | 0.0312 | 0.0578 | 0.0882 | 0.0556 | 0.0556 | 4 |
| | C Sa M | 1 | 56.90 | 55.00 | 55.43 | 55.60 | - | - | |
| | | 2 | 56.88 | 54.79 | 55.41 | 56.20 | - | - | |
| | | Variance | 0.0002 | 0.0420 | 0.0002 | 0.1800** | 0.0506 | 0.0075 | 3 |
| | Unc D | 1 | 79.06 | 77.75 | 77.40 | 78.98 | - | - | |
| | | 2 | 79.14 | 75.90 | 77.59 | 79.00 | - | - | |
| | | Variance | 0.0032 | 1.7112** | 0.0180 | 0.0002 | 0.4332 | 0.0072 | 3 |
| C | FA III | 1 | 37.12 | 34.14 | 34.86 | 37.48 | - | - | |
| | | 2 | 38.10 | 34.56 | 33.92 | 37.34 | - | - | |
| | | Variance | 0.4802 | 0.0072 | 0.4418 | 0.0098 | 0.2348 | 0.2348 | 4 |
| | Pum P | 1 | 65.10 | 64.49 | 69.93 | 65.12 | - | - | |
| | | 2 | 64.82 | 64.60 | 68.72 | 65.16 | - | - | |
| | | Variance | 0.0392 | 0.0060 | 0.7320 | 0.0008 | 0.194[illegible] | 0.1945 | 4 |
| | C Sa M | 1 | 53.50 | 52.61 | 55.07 | 55.10 | - | - | |
| | | 2 | 53.88 | 52.25 | 54.94 | 54.80 | - | - | |
| | | Variance | 0.0722 | 0.0648 | 0.0084 | 0.0450 | 0.0476 | 0.0476 | 4 |
| | Unc D | 1 | 76.14 | 75.00 | 77.07 | 79.30 | - | - | |
| | | 2 | 76.42 | 74.60 | 77.36 | 79.10 | - | - | |
| | | Variance | 0.0392 | 0.0800 | 0.0420 | 0.0200 | 0.0453 | 0.0453 | 4 |

* Since two results were obtained by each laboratory, the pooled variance is equal to the average of the within-laboratory variances and 4 degrees of freedom are associated with it.

** Rejected by Bartlett Variance Test at the 95% confidence level.

Table 3

$R_2O_3$ Test Results

| Method | Material | Test Run | $R_2O_3$ in Percent as Measured at Laboratory 1 | 2 | 3 | 4 | Pooled Variance* | Resultant Pooled Variance After Bartlett Test | Degrees of Freedom Associated with Resultant Variance |
|---|---|---|---|---|---|---|---|---|---|
| A | PA III | 1 | 41.30 | 40.20 | 40.23 | 41.08 | - | - | |
| | | 2 | 41.28 | 40.34 | 40.17 | 41.06 | - | - | |
| | | Variance | 0.0002 | 0.0098 | 0.0022 | 0.0002 | 0.0031 | 0.0031 | 4 |
| | Pum P | 1 | 14.78 | 14.68 | 14.57 | 15.26 | - | - | |
| | | 2 | 14.80 | 14.77 | 14.53 | 15.19 | - | - | |
| | | Variance | 0.0002 | 0.0060 | 0.0008 | 0.0024 | 0.0024 | 0.0024 | 4 |
| | C Sh X | 1 | 15.68 | 14.43 | 15.62 | 16.04 | - | - | |
| | | 2 | 15.82 | 14.37 | 15.74 | 15.80 | - | - | |
| | | Variance | 0.0098 | 0.0018 | 0.0072 | 0.0288 | 0.0119 | 0.0119 | 4 |
| | Unc D | 1 | 9.86 | 9.58 | 9.66 | 10.20 | - | - | |
| | | 2 | 10.00 | 9.41 | 9.75 | 10.26 | - | - | |
| | | Variance | 0.0098 | 0.0144 | 0.0040 | 0.0018 | 0.0075 | 0.0075 | 4 |
| B | PA III | 1 | 41.26 | 43.53 | 40.65 | 41.92 | - | - | |
| | | 2 | 41.08 | 43.83 | 40.89 | 41.80 | - | - | |
| | | Variance | 0.0162 | 0.0450 | 0.0288 | 0.0072 | 0.0243 | 0.0243 | 4 |
| | Pum P | 1 | 14.72 | 17.51 | 14.83 | 15.44 | - | - | |
| | | 2 | 15.24 | 17.65 | 14.63 | 15.62 | - | - | |
| | | Variance | 0.1352 | 0.0098 | 0.0200 | 0.0162 | 0.0453 | 0.0453 | 4 |
| | C Sh H | 1 | 15.86 | 15.63 | 15.70 | 16.02 | - | - | |
| | | 2 | 16.32 | 15.61 | 15.47 | 15.78 | - | - | |
| | | Variance | 0.1058 | 0.0002 | 0.0264 | 0.0238 | 0.0403 | 0.0403 | 4 |
| | Unc D | 1 | 9.52 | 9.87 | 10.14 | 12.24 | - | - | |
| | | 2 | 9.16 | 9.90 | 9.99 | 11.92 | - | - | |
| | | Variance | 0.0648 | 0.0004 | 0.0112 | 0.0512 | 0.0319 | 0.0319 | 4 |
| C | PA III | 1 | 40.30 | 40.63 | 37.43 | 41.14 | - | - | |
| | | 2 | 40.16 | 40.70 | 39.13 | 41.10 | - | - | |
| | | Variance | 0.0098 | 0.0024 | 1.4450** | 0.0008 | 0.3645 | 0.0043 | 3 |
| | Pum P | 1 | 14.64 | 14.55 | 10.31 | 14.76 | - | - | |
| | | 2 | 14.62 | 14.61 | 10.68 | 14.46 | - | - | |
| | | Variance | 0.0002 | 0.0018 | 0.0684 | 0.0450 | 0.0289 | 0.0289 | 4 |
| | C Sh H | 1 | 15.84 | 16.34 | 15.05 | 15.62 | - | - | |
| | | 2 | 15.68 | 16.24 | 15.27 | 15.80 | - | - | |
| | | Variance | 0.0128 | 0.0050 | 0.0242 | 0.0162 | 0.0146 | 0.0146 | 4 |
| | Unc D | 1 | 10.38 | 9.64 | 9.10 | 11.12 | - | - | |
| | | 2 | 9.84 | 9.58 | 8.94 | 10.86 | - | - | |
| | | Variance | 0.1458 | 0.0018 | 0.0128 | 0.0338 | 0.0486 | 0.0486 | 4 |

* Since two results were obtained by each laboratory, the pooled variance is equal to the average of the within-laboratory variances and 4 degrees of freedom are associated with it.

** Rejected by Bartlett Variance Test at the 1% confidence level.

Table 4

MgO Test Results

| Method | Material | Test Run | MgO in Percent as Measured at Laboratory 1 | 2 | 3 | 4 | Pooled Variance* | Resultant Pooled Variance After Bartlett Test | Degrees of Freedom Associated with Resultant Variance |
|---|---|---|---|---|---|---|---|---|---|
| A | FA III | 1 | 0.76 | 0.11 | 0.83 | 0.81 | - | - | |
| | | 2 | 0.85 | 0.12 | 0.83 | 0.86 | - | - | |
| | | Variance | 0.0040 | 0.0001 | 0 | 0.0012 | 0.0013 | 0.0013 | 4 |
| | Pum F | 1 | 0.19 | 0.00 | 0.09 | 0.19 | - | - | |
| | | 2 | 0.22 | 0.00 | 0.11 | 0.17 | - | - | |
| | | Variance | 0.0004 | 0 | 0.0002 | 0.0002 | 0.0002 | 0.0002 | 4 |
| | C Sh M | 1 | 2.68 | 1.70 | 2.78 | 3.14 | - | - | |
| | | 2 | 2.79 | 1.61 | 2.82 | 3.11 | - | - | |
| | | Variance | 0.0060 | 0.0040 | 0.0008 | 0.0004 | 0.0028 | 0.0028 | 4 |
| | Unc D | 1 | 0.67 | 0.00 | 0.71 | 1.25 | - | - | |
| | | 2 | 0.68 | 0.00 | 0.75 | 1.29 | - | - | |
| | | Variance | 0.0001 | 0 | 0.0008 | 0.0008 | 0.0004 | 0.0004 | 4 |
| B | FA III | 1 | 0.90 | 0.05 | 0.81 | 0.83 | - | - | |
| | | 2 | 0.99 | 0.06 | 0.81 | 0.85 | - | - | |
| | | Variance | 0.0040 | 0.0001 | 0 | 0.0002 | 0.0011 | 0.0011 | 4 |
| | Pum F | 1 | 0.13 | 0.00 | 0.16 | 0.18 | - | - | |
| | | 2 | 0.14 | 0.00 | 0.25 | 0.16 | - | - | |
| | | Variance | 0.0001 | 0 | 0.0040 | 0.0002 | 0.0011 | 0.0011 | 4 |
| | C Sh M | 1 | 3.02 | 1.61 | 2.97 | 2.75 | - | - | |
| | | 2 | 2.58 | 1.74 | 2.90 | 2.73 | - | - | |
| | | Variance | 0.0968** | 0.0084 | 0.0024 | 0.0002 | 0.0270 | 0.0037 | 3 |
| | Unc D | 1 | 0.67 | 0.02 | 0.83 | 0.74 | - | - | |
| | | 2 | 0.64 | 0.01 | 0.79 | 0.72 | - | - | |
| | | Variance | 0.0004 | 0.0001 | 0.0008 | 0.0002 | 0.0004 | 0.0004 | 4 |
| C | FA III | 1 | 0.74 | 0.04 | 0.88 | 0.75 | - | - | |
| | | 2 | 0.80 | 0.06 | 0.81 | 0.75 | - | - | |
| | | Variance | 0.0018 | 0.0002 | 0.0024 | 0 | 0.0011 | 0.0011 | 4 |
| | Pum F | 1 | 0.12 | 0.02 | 0.23 | 0.15 | - | - | |
| | | 2 | 0.06 | 0.02 | 0.28 | 0.13 | - | - | |
| | | Variance | 0.0018 | 0 | 0.0012 | 0.0002 | 0.0008 | 0.0008 | 4 |
| | C Sh M | 1 | 2.95 | 1.80 | 2.01 | 2.65 | - | - | |
| | | 2 | 2.99 | 1.93 | 1.97 | 2.69 | - | - | |
| | | Variance | 0.0008 | 0.0084 | 0.0008 | 0.0008 | 0.0027 | 0.0027 | 4 |
| | Unc D | 1 | 0.53 | 0.02 | 0.42 | † | - | - | |
| | | 2 | 0.69 | 0.01 | 0.42 | † | - | - | |
| | | Variance | 0.0128** | 0.0001 | 0 | - | 0.0043 | 0.0001 | 2 |

* Since two results were obtained by each laboratory, the pooled variance is equal to the average of the within-laboratory variances and 4 degrees of freedom are associated with it (except for Method C Unc D).

** Rejected by Bartlett Variance Test at the 95% confidence level.

† Results not reported.

Table 5

Calculated Error Variance for Methods

| Constituent | Method | Calculated Error Variance FA III | Pum F | C Sh M | Unc D | Pooled Variance | Degrees of Freedom Associated with Pooled Variance | Resultant Pooled Variance After Bartlett Test | Degrees of Freedom Associated with Resultant Variance |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | A | 0.0055 | 0.0146 | 0.0478 | 0.0706 | 0.0346 | 16 | 0.0346 | 16 |
| | B | 0.0019 | 0.0556* | 0.0075 | 0.0072 | 0.0209 | 13 | 0.005[illegible] | 9 |
| | C | 0.2348 | 0.1945 | 0.0476 | 0.0453 | 0.1306 | 16 | 0.1306 | 16 |
| $R_2O_3$ | A | 0.0031 | 0.0024 | 0.0119 | 0.0075 | 0.0062 | 16 | 0.0062 | 16 |
| | B | 0.0243 | 0.0453 | 0.0403 | 0.0319 | 0.0354 | 16 | 0.0[illegible]5 | 16 |
| | C | 0.0043 | 0.0289 | 0.0146 | 0.0486 | 0.0254 | 15 | 0.0254 | 15 |
| MgO | A | 0.0013 | 0.0002 | 0.0028 | 0.0004 | 0.0012 | 16 | 0.0012 | 16 |
| | B | 0.0011 | 0.0011 | 0.0037 | 0.0004 | 0.0014 | 15 | 0.0014 | 15 |
| | C | 0.0011 | 0.0008 | 0.0027 | 0.0001 | 0.0013 | 14 | 0.0013 | 14 |

* Rejected by Bartlett Variance Test at the 95% confidence level.

Table 6

Calculated Error Variance for Constituents

| Constituent | Calculated Error Variance Method A | Method B | Method C | Pooled Variance | Degrees of Freedom Associated with Pooled Variance | Resultant Pooled Variance After Bartlett Test | Degrees of Freedom Associated with Resultant Variance |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 0.0346* | 0.0055 | 0.1306* | 0.0656 | 41 | - | - |
| $R_2O_3$ | 0.0062* | 0.0354 | 0.0254 | 0.0223 | 47 | 0.0306 | 31 |
| MgO | 0.0012 | 0.0014 | 0.0013 | 0.0013 | 45 | 0.0013 | 45 |

* Rejected by Bartlett Variance Test at the 95% confidence level.

Table 7

Comparison of Error Variances

| Constituent | Calculated Error Variance Determined in Present Study | | | Error Variances Calculated from Standard Deviations Reported* in NBS Interlaboratory Test of Portland Cement | |
|---|---|---|---|---|---|
| | Method A | Method B | Method C | $(a/2)^2$ | Average Variance of 12 Samples |
| $SiO_2$ | 0.0346 | 0.0055 | 0.1306 | 0.0072 | 0.0576 |
| $R_2O_3$ | 0.0062 | 0.0306 | 0.0306 | 0.0169** | 0.1296** |
| MgO | 0.0013 | 0.0013 | 0.0013 | 0.0049 | 0.0400 |

* Crandall and Blaine.[1]

** Values reported for $Al_2O_3$.

Table 8

Laboratory Scores Obtained by Ranking Laboratory Results

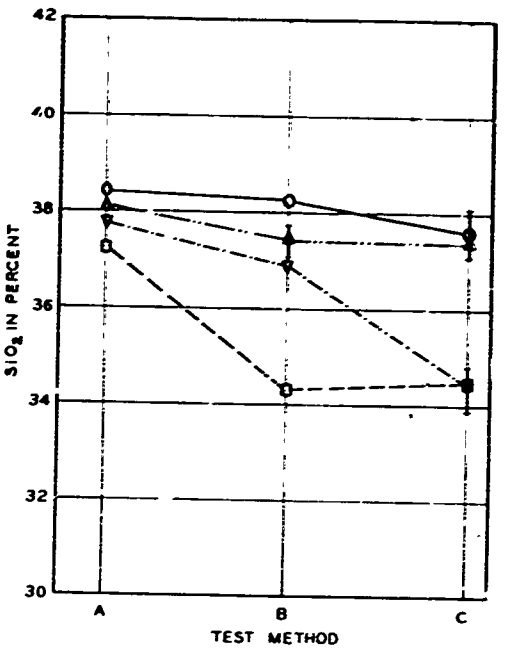
| Constituent | Method | Laboratory Scores* Lab 1 | Lab 2 | Lab 3 | Lab 4** | Ratio of Calculated to Expected Sums of Squares S/S'† |
|---|---|---|---|---|---|---|
| $SiO_2$ | A | 5 | 15 | 13 | 7 | 3.4†† |
| | B | 4†† | 16†† | 11 | 9 | 3.7†† |
| | C | 10 | 15 | 8 | 7 | 1.9 |
| $R_2O_3$ | A | 8 | 13 | 14 | 5 | 2.7†† |
| | B | 11 | 8 | 14 | 7 | 1.5 |
| | C | 8 | 9 | 16†† | 7 | 2.5 |
| MgO | A | 10 | 16†† | 9 | 5 | 3.1†† |
| | B | 9 | 16†† | 6 | 9 | 2.7†† |
| | C | 7 | 16†† | 8 | 9 | 2.5 |

* The minimum score that can be obtained by any laboratory is 4, and the maximum score is 16. Both of these scores are significant at the 5% probability level. A score of 4 means that the laboratory had the highest results in the analysis of all four materials; a score of 16 signifies that the laboratory had the lowest results in the analysis of all four materials.

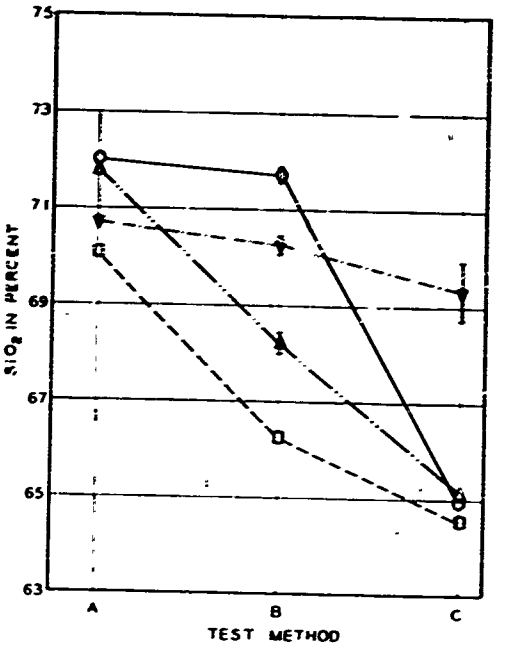
** Test results were assumed for laboratory 4 for the analysis of MgO in Unc D by Method C.

† The average expected score is 10, and the expected sum of squares (S') is 20. An S/S' ratio of 2.60 is significant at the 5% probability level and a ratio of 3.78 is significant at the 1% probability level.

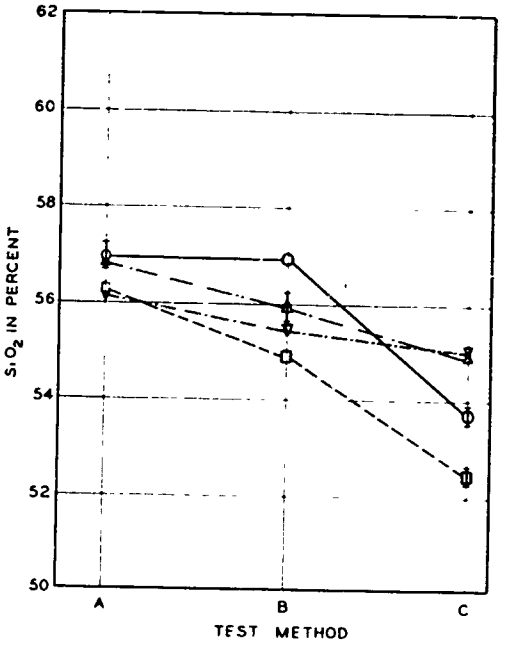
†† Significant at the 5% probability level.



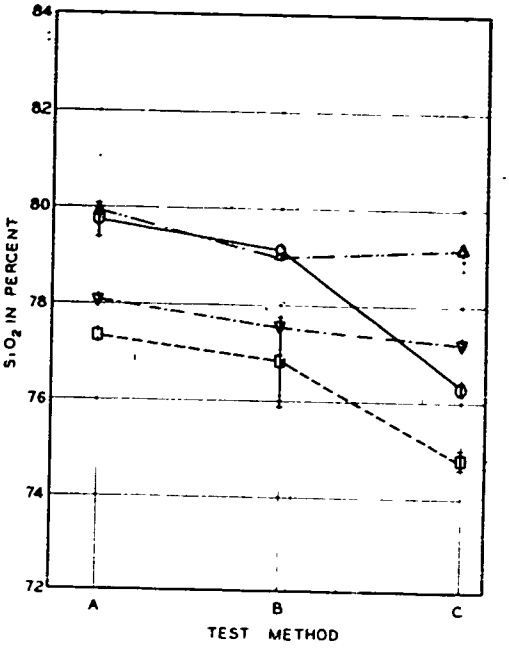

FA III




Pum F




C Sh M




Unc D

LEGEND

- LABORATORY 1
- LABORATORY 2
- LABORATORY 3
- LABORATORY 4
- RANGE OF TESTS

NOTE POINTS INDICATE THE AVERAGES OF TWO TESTS

$SiO_2$ TEST RESULTS

PLATE I

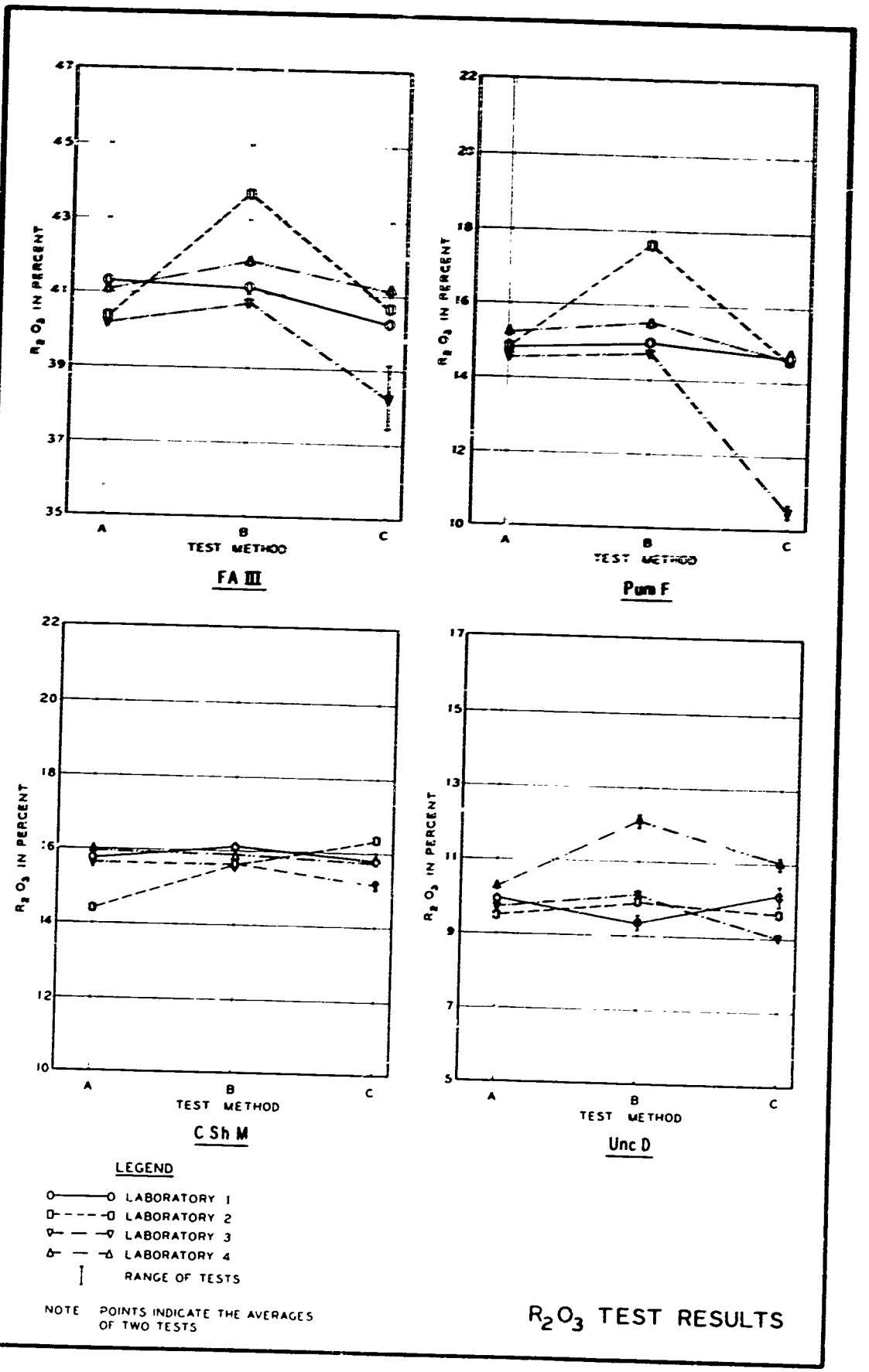

47
45
43
41
39
37
35
$R_2O_3$ IN PERCENT
A
B
C
TEST METHOD
FA III
22
20
18
16
14
12
10
$R_2O_3$ IN PERCENT
A
B
C
TEST METHOD
Pum F
22
20
18
16
14
12
10
$R_2O_3$ IN PERCENT
A
B
C
TEST METHOD
C Sh M
17
15
13
11
9
7
5
$R_2O_3$ IN PERCENT
A
B
C
TEST METHOD
Unc D
LEGEND
LABORATORY 1
LABORATORY 2
LABORATORY 3
LABORATORY 4
RANGE OF TESTS
NOTE POINTS INDICATE THE AVERAGES OF TWO TESTS
$R_2O_3$ TEST RESULTS

PLATE 2

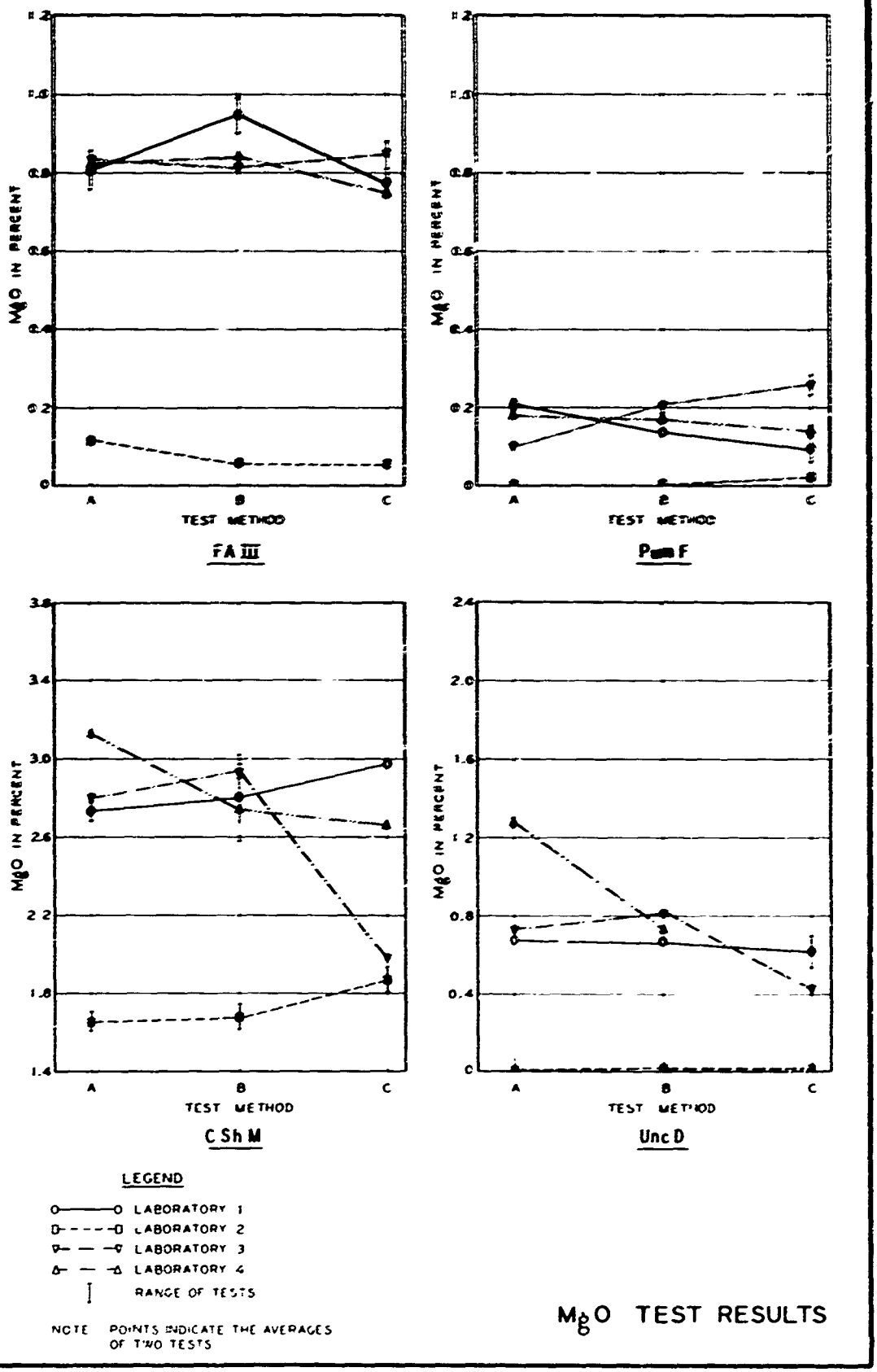

MgO IN PERCENT
TEST METHOD
A
B
C
FA III
Pum F
C Sh M
Unc D
LEGEND
LABORATORY 1
LABORATORY 2
LABORATORY 3
LABORATORY 4
RANGE OF TESTS
NOTE POINTS INDICATE THE AVERAGES OF TWO TESTS
MgO TEST RESULTS

PLATE 3